Size-Distributions and Mixtures of Black Carbon and Dust Aerosol in Asian Outflow: Physio-chemistry, Optical Properties, and Implications for CCN

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Aircraft measurements during TRACE-P and ACE-Asia described the properties of the size distribution of Asian aerosol, the state of mixing, light absorbing properties and the role of Black Carbon (BC) and other aerosol constituents in combustion and/or dust plumes. Optical particle sizing in association with thermal heating resolved refractory aerosol sizes (those remaining at 300°C and dominated by soot and dust or sea-salt) from volatile constituents (associated with more soluble species) for diameters, D_p, from 0.010 μm to over 10 μm. These optically effective sizes (OES) and associated measured optical properties constrain the dust refractive index to near 1.53-0.0005i, yielding a single scatter albedo, ϖ (550nm), near unity for $D_p<1$ μm to about 0.9 at $D_p=$ 10 μm and with overall values during these campaign of near 0.97. The effective mass absorption efficiency, MAE, for typical dust distributions was estimated at 0.012 ±0.003 m^2g^{-1}. Less dust south of 25°N and stronger biomass burning signatures than those to the north resulted in lower values for ϖ near 0.82. Measured elemental carbon (EC) showed considerable variability ($R^2 = 0.25$) relative to BC light absorption while refractory volumes (soot sizes from 0.1-0.5 μm) were highly correlated ($R^2 = 0.74$) with absorption from BC. Both approaches suggest a range of MAE for BC of about 8.5±3m^2g^{-1} with some of this variability influenced by the state of mixing of the aerosol. Soot and BC was usually internally mixed with volatile aerosol and generally constituted about 10-30% of the accumulation mode mass but was present in typically 75% of the total particle number. The mass fraction of BC in the accumulation mode was highest in the presence of dust due the competing uptake of condensates like sulfate and organic carbon, OC, onto the coarse dust surface. This lowered ϖ values for the accumulation mode from about 0.84 in pollution to about 0.76 in peak dust events. Coarse particle absorption was often enhanced by up to 20% of the total due to BC also becoming attached to the dust surface. The uptake of soluble species onto BC also implies that BC establishes the majority of the optically active aerosol particles and most of the cloud condensation nuclei, CCN. The Aerosol Index (product of aerosol scattering and Angstrom exponent) correlates with these inferred CCN and provides support for estimating these CCN from satellite.

1. Introduction

BC has a strong light absorption per unit mass (or mass absorption efficiency - MAE) and submicrometer (hereafter called sub-µ) refractory dust has much lower MAE. It is well known that the light absorbing BC mass is generally found in the sub-µ sizes while most dust mass is in supermicrometer sizes. The radiative properties of atmospheric aerosol depend upon the size and nature of the mixing of these absorbers with other common atmospheric aerosol such as sulfates, ammonium, nitrates, organic carbon and water. These mixtures range between internal (multiple components within a particle) and external (different components in different particles). Since many of the components are hygroscopic and take up water as a function of relative humidity (RH) then the nature of the soluble and insoluble components of the mixtures determine the size, refractive index and optical properties under ambient RH conditions. Hence, efforts that include the modeling of aerosol radiative properties or the retrieval of aerosol properties from optical measurements need to properly account for the size, composition, state of mixing, refractive indices and water uptake (soluble and insoluble components) of the aerosol.

The representative ambient complex refractive index of atmospheric soot, BC and dust is an essential parameter for modeling their light absorption but remains poorly characterized. Soot can be a complex mix of components including highly absorbing BC. The influence of size, morphology, aggregation, composition, refractive index and other characteristics influencing BC optical properties are discussed in the excellent paper by Fuller, Malm and Kriedenweiss (1999), hereafter referred to as FMK. Dust optical properties can exhibit different characteristics for similar reasons. Sokolik and Toon [1999] suggest that the imaginary part of dust with 1% hematite lie somewhere near 0.001 at a wavelength of 0.55 um. Kalashnikova and Sokolik [2002] use this value in their model and yield a range of single scatter albedo between 0.969 and 0.978 depending on the dust shape for an assumed lognormal distribution with a number median diameter of 1 um. These simulated single scatter albedo values are in good agreement with in situ observations by Anderson et al. [2003], Clarke et al. [2001], and Kaufman et al. [2001].

In this paper we will focus attention upon the absorbing properties of dust and BC. These will be discussed in conjunction with characteristics of the accumulation and coarse mode aerosol, the soot component of the aerosol and concurrent EC measurements. Hence, it is important to clarify these terms in this paper. BC is used here as the light absorbing component of the soot aerosol. We use the word "soot" here to represent the combination of BC with other species emitted near the combustions source that might be mixed with it such as fly ash, OC, or pyrolized and unburnt fuel etc. At times "soot/BC" will be used to emphasize this link. Because most of our samples were hours to days away from the combustion source this evaluation reflects aged soot emissions often associated with other condensates that largely comprise what we refer to as the sub-µ accumulation mode.   The term EC is retained for the operationally defined carbon mass concentration inferred from the evolution of CO_2 detected upon sample filter combustion (Bertram et al., submitted 2003).

The optically effective sizes (OES) of the aerosol measured and discussed here range from the lower end of the accumulation mode near 0.1 µm to the larger end of the dust mode near 10 µm. These include primary emissions of soot, fly ash, dust, sea-salt and secondary aerosol components such as sulfates, nitrates and organic carbon etc. Variations in the degree of internal and external mixes of these aerosol components

determine their spectral radiative effects. The production, transport and removal of these aerosol are also size dependent upon and often coupled to meteorological processes. As a result, both-size resolved and species-resolved physical, chemical and optical properties are needed if these processes are to be parameterized in chemical transport models or coupled to satellite retrievals of aerosol properties.

During spring of 2001 we participated in two aircraft experiments as part of NASA TRACE-P (Jacob et al., 2003) and ACE-Asia (Huebert et al., 2003) studying the properties of Asian aerosol advected over the North Pacific. These sequential experiments with nearly identical instrumentation provided a unique opportunity to investigate outflow from East Asia between 5N and 50N during the same season. The TRACE-P experiment (Feb. 24,2001-April 10, 2001) were initially based in Hong Kong and after March 17 were based in Yakota, Japan. ACE-Asia flights were based out of Iwakuni Japan from March 31st to May 4th 2001 . The last two TRACE-P flights out of Yakota were flown in conjunction with the first two ACE-Asia flights flown out of Iwakuni, Japan allowing us to quantitatively compare instrumentation on both aircraft. All ACE-Asia measurements were made using the Low Turbulence Inlet (LTI) and the P3B measurements employed our shrouded solid differ inlet, both of which were evaluated in the PELTI experiment (Huebert et al, 2002). Our instrumentation and most other aerosol instruments were in good agreement (Moore et al., 2003) allowing us to combine data sets from both experiments and extend our observations both spatially and temporally.

2. Instrumentation

The aircraft aerosol data discussed here include measurements of number, size, composition, and optical properties along with other related measurements including gas phase species. These include:

- Aerosol size distributions obtained from a laser optical particle counter (OPC) . a modified LAS-X (PMS, Boulder, Co.).   The aerosol volume distributions obtained from the OPC are the sizes that dominate aerosol scattering and are measured as optical effective sizes (OES). Calibration particles had a refractive index of 1.588 up to 2 μm and 1.54 above that. The fact that the OPC measures scattering means it provides a first order shape correction. This makes OES distributions most useful for modeling optical properties, as done in this paper, but size adjustments for optical effects should be made when comparing to actual measured mass and mass dependent properties. Composition information can also be used to adjust these sizes for other refractive indices (e.g. wet or absorbing aerosol) when making these calculations.
- The OPC was operated with thermo-optic aerosol discriminator (TOAD) in order to infer size dependent volatility by cycling aerosol through heaters at 150°C and at 300°C to resolve the remaining refractory aerosol. These refractory aerosol sizes include most light-absorbing soot (and Black Carbon -BC) below about 1μm while the larger refractory component is generally dust or occasionally sea-salt in these experiments near Asia. Our choice for thermal analysis included heating to

150°C is designed to drive off sulfuric acid and heating to 300°C is designed to volatilize ammonium sulfate (Clarke, 1991).

- A Radial differential mobility analyzer (DMA) provided size information down to about 0.007 μm. Dual DMA's were also operated in a Tandem DMA mode (TDMA) with similar thermal analysis. One DMA selects a size for thermal conditioning before resizing with a second DMA. However, because the procedure takes about 5min and because the more rapid DMA measurements are not possible at this time the TDMA scans were only intermittently performed. Samples collected over 20s are taken into a lagged aerosol grab (LAG) chamber for subsequent DMA analysis. The DMA included the thermal analysis similar to the OPC but also incorporated the TDMA capability described above. This allows details of the aerosol volatility to be observed by heating and individual size class selected from that mode to determine how sizes and concentrations were affected. If the integral mass decreases a lot upon heating but the integral number does not then this indicates that the particles were internally mixed and that the refractory components were probably a condensation site for the volatile components.

- Aerosol number concentrations were measured at 1Hz with an Ultrafine Condensation Nuclei counter (UCN; TSI 3025) and CN counters (TSI 3760, TSI 3010) operated at 40 and 360°C. The latter can reveal the refractory number concentration of the aerosol that often provides a rapid indication of air mass character not always evident in the total concentration (Clarke et al., 1997)

- Two TSI 3563 3-wavelength nephelometers were used on ACE-Asia to measure continuous coarse and fine aerosol scattering during ACE-Asia. One drew air through a 1 μm impactor [Anderson et al., 2002]. TRACE-P employed a single TSI nephelometer with the same model impactor cycled sequentially to get total and sub-μ light scattering. Angular truncation corrections for the TSI nephelometer were applied to data shown here (Anderson et al., 1996).

- Light absorption from Particle Soot Absorption Photometers (PSAP, Radiance Research) was used on both experiments with and without a 1μm impactor. Corrections for artifact absorption due to scattering were applied after Bond et al. (1999). In conjunction with the nephelometry this also established coarse and fine aerosol single scatter albedo. On TRACE the PSAP operated at about 4-5 lpm resulting in impaction losses of about 50% for 4 μm particles while on ACE it was operated at 1 lpm resulting in impaction losses of 50% at 12.5 μm [Y. Shinozuka, personal correspondence]. This will result in some underestimates of total coarse dust absorption for both experiments. Although the higher flow rate makes losses potentially greater on TRACE, the fact that we rarely encountered pronounced dust events on TRACE means that this effect was seldom significant.

- Fast ion-chromatography from a Particle in Liquid Sample (PILS, Weber et al., 2001; Orsini et al., 2003) was also employed and compared with aerosol volatility to resolved variations in soluble [eg. sulfate, nitrate]and refractory species [eg. dust, BC] that could influence f(RH) with about 4 minute (20km) horizontal resolution.

- Elemental Carbon and Organic Carbon, operationally defined measures of BC and OC based upon the thermal evolution of CO_2, was measured on the ACE-Asia aircraft (Huebert et al. 2002, Bertram et al., 2003).

An important feature of our measurements on ACE-Asia and TRACE-P was the periodic thermal heating of the aerosol prior to analysis by both the DMA and OPC instruments. The volatility of the aerosol is a physio-chemical property of the aerosol related to its size dependent composition. These measurements are made on relatively dry aerosol sizes so size variability due simply to water uptake is minimized. This makes size corrections small for refractive index effects for non-absorbing aerosol and readily accomplished. Hence, these combined techniques can provide insight into physiochemistry, transformations and related processes affecting the radiative and cloud nucleating properties of the Asian aerosol. This approach has been used in the remote marine environment to infer the sub-μ sulfate and its relative neutralization by ammonium for values of the molar ratio of ammonium to sulfate between 0 and 1 (Clarke et al., 1991). However, in the polluted and varied Asian aerosol this simple interpretation of volatile constituents is less clear. Nevertheless, we will demonstrate that the volatility can be effectively interpreted in association with related chemical measurements. The mass and number of primary particles in both fine and coarse sizes (soot, flyash, sea-salt, dust) are separable from volatile and condensed sulfates, nitrates and OC present in different size classes. Volatility information can also be augmented by linking these observations to aerosol chemistry, optical properties, and response to changing humidity, f(RH).

3. The TRACE-P and ACE-Asia experiments

Comparison of data sets from different experiments can often be problematic due to different instrumentation or sampling approaches. Consequently, deliberate efforts at side-by-side flights were made both between the TRACE-P P3B and the ACE-Asia C-130 during the few days these two experiments overlapped. A detailed evaluation of these airborne aerosol measurements is made elsewhere (Moore et al., 2003). In spite of differences in inlet types the agreement in aerosol sizing and optical properties were good at all altitudes and provides confidence that these and the related optical measurements discussed here are comparable and can be integrated. A comparison of average vertical profiles for scattering, absorption and ϖ for the measured dry aerosol are shown in Figure 2 for all TRACE-P and ACE-Asia flights.

3.1   Spatial variability in absorption on ACE-Asia and TRACE-P

A sense of the flights and data coverage for both experiments is reflected in the measurements of light absorption (or BC) as illustrated in Figure 1. This includes the latitude-longitude coverage of the data and vertical vs. latitude presentation for data both above and below 3km during both experiments. Significant aerosol absorption is common throughout both study regions in the lowest 3km, but the logarithmic scale illustrates that both low and high absorption were encountered. The highest values were

often elevated in and near the Yellow Sea. This region is generally downwind of many major cities and sources of sulfates and associated combustion emissions (Carmichael et al., 2003, Jacob et al., 2003). However, concentrations vary with sources from regional scales, urban center scales and down to plume scales of several km. Regionally, the data from TRACE-P south of 25°N tend to have combustion sources often influenced by a biomass signature (Ma et al., 2003) while to the north more urban emissions and coarse dust is often present. Hence, we have broken TRACE-P data into north and south of 25N for comparison with of the ACE-Asia data.

TRACE-P flight data has been separated into data collected south and north of 25°N in view of chemical and meteorological differences evident for these regions (Jacob et al., submitted 2002). Because the 19 ACE-Asia flights were north of 25°N (Figure 1) these are best compared to the 5 TRACE-P flights north of 25°N even though the number of flights, time periods and meteorological conditions differed. The average TRACE-P data south of 25°N (top panels) suggest a high scattering and absorbing layer below 1km with a deeper 1 to 4 km layer above characterized by moderate scattering but high absorption with transitions to lower and more typical values for both above 4km. The associated profile for ϖ shows the highest values near 0.9 at the surface that drop to about 0.8 near 2 km. The values for ϖ continue to vary about that value up to altitudes of 6km. This is a result of the absorbing plume evident between 1 and 4 km often associated with elevated chemical signatures associated with biomass burning (Ma et al., 2003).

The data north of 25°N from both TRACE-P (middle panels) and ACE-Asia (lower panels) reveal generally similar behavior but differ from the data south of 25N. Both TRACE-P and ACE-Asia do show high scattering and absorption values below 1 km but exhibit trends to lower values aloft. The greatest difference is for ϖ north of 25°N that has values near 0.9 at the surface but increases with altitude to values near 0.95 at 6 km. As discussed below, this increase is largely due to the presence of dust aerosol characterized by a high ϖ near 0.97 for this region. The more numerous ACE-Asia flights and greater frequency of the dust events during ACE-Asia contribute to the higher and more stable average scattering and absorption aloft for ACE-Asia data. Even so, average near surface properties of the aerosol for all 3 examples reveal ϖ values all near 0.9. This similarity in surface ϖ over space and time emphasizes the importance of aircraft data in establishing aerosol and optical properties over the atmospheric column since these surface data provide a poor representation of the column properties in both regions.

These average profile data are a result of numerous flights that exhibit far greater structure than Figure 2 suggests. An example of this 3 dimensional variability in size, composition and optical properties are demonstrated in Figure 3 for TRACE-P flight 16 (March 29, 2001) that included several profiles over the Sea of Japan and others to the east of Japan. Accumulation mode (pollution) and coarse mode (dust) aerosol are generally mixed at the surface but the spatial variation in aerosol properties is large. Careful examination of these plots reveals that the contributions to absorption and scattering arise from accumulation mode aerosol and coarse mode aerosol that generally exhibit peak values at different altitudes and locations. Surface aerosol properties, such as ϖ shown in the average profiles in Figure 2, also fail to properly characterize the major plume transport or column values representative of optical properties represented in

satellite retrievals of column values. Absorption values at the surface east of Japan and to the north are related to accumulation mode aerosol volume (V-acc) but are mixed with contributions related to coarse mode dust volume (V-coarse) aloft near 1km altitude. Dust plumes present between 1 and 3 km to the north end of the Sea of Japan are associated with low accumulation mode volume and low sulfate such that scattering and absorption are dominated by dust. This is also true for a separate dust plume at 5km altitude evident to the east of Japan.

This 3-D variability in relative constituents is also present in the ratios of coarse to total surface areas. Aerosol surface area is both a location for heterogeneous chemical reactions and condensation as well as being instrumental in the coagulation of smaller aerosol with larger ones. Hence, this variability can affects both gas phase concentrations and the evolving aerosol size-distribution including their associated optical effects. High ϖ is evident in low aerosol regions and in dust while low ϖ values are present in more polluted regions. This variability in three dimensions means that rapid measurements are needed to properly characterize the aerosol. Our size distributions were generally accumulated between 30 s to 2 min so that reasonable stratification of data can be made to characterize this variability.

3.2 Size Distributions and Volatility

Several examples of OPC thermally-resolved size-distribution data from Flight 13 of ACE-Asia are shown in Figure 4 for diameters between 0.1 and 10 μm. This flight was selected because it included very high dust concentrations mixed with soot and it will be referred to repeatedly in this paper. This size range generally encompasses most aerosol mass that influences aerosol radiative effects at visible wavelengths. The high dust cases provide constraints on the dust optical properties. OPC data here and elsewhere are presented as dry optically effective sizes (OES) unless otherwise indicated. These sizes are somewhat larger than actual size due to shape effects discussed later and conversion to estimated mass also assumes a density of 2.5 g cm^{-3}. Each case reflects an average of about 15-20 OPC distributions accumulated under similar conditions so that volatility behavior is robust and not a result of concentration variations over a single 90 sec OPC cycle period. These are presented in a logarithmic format to expose the full range of concentrations and also as linear volume distributions (where the area under each curve is proportional to volume) in order to better reveal relative contributions. The top row illustrates a moderate dust event associated with low measured sub-μ light absorption. A small amount of volatility is evident between 150°C and 350°C for the accumulation mode present between 0.1 and 0.5 μm. In a less polluted environment this would suggest about 0.5 μg m^{-3} neutralized sulfate with little sulfuric acid present (Clarke, 1991) but here other volatile components may play a role. Some nitrates or volatile OC can possibly contribute to components volatile at 300°C but comparisons to chemistry (see below) suggest sulfate is a common constituent. The refractory dust is shown as a linear volume distribution (area under plot proportional to volume) in the top middle panel corresponding to about 125 μg m^{-3} and the volatile component is no longer resolvable for this mode. The logarithmic plot (right) represents this refractory "dust" OES size distribution between 0.1 μm and 10 μm after the non-absorbing volatile species

were removed. In fact, some residual soot remains even in this "clean" dust case and contributes to some of this number (see more extensive discussions in section 3.3). Nevertheless, this approach of removing the volatile component to reveal the dust size-distribution allows us to constrain the complex refractive index of this aerosol.

The middle row in Figure 4 illustrates a high dust concentration mixed with a significant amount of pollution aerosol. The linear volume plot suggests significant volume in the dust mode above 10 μm diameter indicating that the total mass is on the order of 1,000 μg m^{-3} as detected by the OPC. The volatile accumulation mode mass is now about 4 μg m^{-3}, an order of magnitude larger than the upper row but still not evident on this linear plot due to the very high dust concentration. However, note the relative increase in refractory volume (300°C) evident on the logarithmic plot below 0.5μm for this case. Most of this is refractory component is combustion soot including BC, as we have observed in other polluted regions (Clarke et al, 1997) and will show below. On the rightmost panel for this case we have taken the shape of the dust mode below 0.6 μm estimated from the top panel and scaled (normalized) it to the refractory concentration at 0.6 μm. We have used it to extend the expected refractory dust-only distribution to smaller sizes (red line) for this high dust case. This example illustrates how subtraction of this refractory dust distribution from the total refractory distribution allows us to resolve the separate refractory mode evident below 0.6 μm (the black plot in the rightmost panel).

The bottom row in Figure 4 is a low dust case associated with a moderate sub-μ light absorption coefficient and moderate volatile component (similar to most TRACE-P data). The amount of volatile accumulation mode mass is about 25 μg m^{-3} (about 3 times the previous case) while the coarse particle dust is only about 50 μg m^{-3} (less than 5% of the previous case). At these concentrations both modes are well resolved on the linear volume plot (center panel) and are also representative of the distributions commonly measured on TRACE-P. The heated size distributions reveal most volatility is present for sizes below about 0.6 μm. However, unlike the previous two cases, the volatile components are also a significant fraction of the coarse mode volume and suggest the accumulation of volatile coatings on the coarse dust aerosol. Because of low count statistics for particle sizes above 5 μm the apparent differences in volatility for these larger sizes are not meaningful. Later we will relate volatile volume to the soluble aerosol fraction but here we will continue to focus upon the refractory (300°C) distribution. Note that the leftmost panel shows that the relative increase for the refractory mode present between 0.1 and 0.5 μm is even more pronounced than for the very high dust case (middle panel). The center panel clearly shows the linear volume peak of this refractory-mode between 0.1 and 0.4 μm that is not evident in the similar plots of the dust modes for the two other cases. Clearly, this mode is not related to the dust distribution but with the accumulation mode pollution component. Proceeding as described above for the high dust case, we have separately resolved the refractory dust mode (red), the refractory accumulation mode (black) and the volatile volume distribution (green) in the panel on the right.

3.3   Distributions of refractory soot and dust

These observations demonstrate that the refractory distribution often consists of a dust distribution along with a separate sub-μ refractory mode that varies independently of the dust mode. In Figure 5 we generalize these observations for the entire ACE-Asia data set collected in the presence of dust concentrations exceeding about 40 μg m^{-3} in order to identify characteristics of the dust mode and the refractory soot (BC) mode. These represent 10 min averages for all periods when OPC thermal analysis was undertaken but only the refractory OES distributions are shown. The top panel reveals that these distributions exhibit several distinctive features. Sizes below about 0.6 μm show variability over two orders of magnitude. Between 0.6 μm and 2.0 μm most distributions have very similar slopes and vary within about one order of magnitude. The curves tend to diverge more at larger sizes, approaching 3 orders of magnitude at the largest sizes. Variability in the refractory accumulation mode is driven largely by soot/BC, as will be discussed below. The greater variability at the largest dust sizes is a result of the sensitivity of these sizes to the production and removal processes. Sizes near one micrometer are resistant to removal processes and change less over time and distance from source (Schütz, 1980).

The distributions highlighted in Figure 5 are for the ACE-Asia flight 13 that experienced the highest dust cases mixed at times with moderate pollution and soot aerosol. Data from three legs flown at 5,500 m, 700 m and 250 m are indicated since these will be used to illustrate the roles of soot and dust in various discussions that follow. It is evident on this plot that the highest dust concentrations are present at the 250 m leg where the refractory accumulation mode (soot) volume has intermediate values. At 700 m the dust mode is less than a factor of two lower while the soot mode is about a factor of 5 lower. At 5,500 m the larger dust sizes decrease again by over an order of magnitude while sizes near 2 μm decrease by a factor of 2 to 3 and the soot near 0.2 μm decrease by a factor of 4 or so. These three sequential legs range from the highest to relatively low dust cases and moderate to lowest soot cases and illustrate the range of aerosol mixes seen during ACE-Asia.

The relative invariance of the slope of the dust mode below 2 μm suggests that the shape of the typical dust distribution might be approximated. Using this shape scaled to a diameter larger than the soot mode allows the refractory soot and dust modes to be separately described. The choice of a diameter for normalizing the distributions should lie in the 0.6 to 2 μm range and preferably lie to the smaller end of this range to minimize the rapidly decreasing count statistics for larger particle sizes.   It was found that favorable results were obtained by normalizing at sizes between about 0.75 to 1.0 μm. Because 0.75 μm OES is about the same as the 1 μm aerodynamic size cut (assuming a density of 2 μg m^{-3}) used for various size segregating impactors on ACE-Asia, including the nephelometers (Anderson et al., 2003), we elected to use that diameter for normalization.

The middle panel in Figure 5 shows the effect of this normalization. The variability in the dust mode is greatly reduced up to sizes of about 3 μm while the soot mode maintains a spread over about 2 to 3 orders of magnitude. The flight 13 legs at 250 m and 700 m now fall on top of each other at the larger sizes while the leg at 5,500 m bounds the lower range of dust cases included here and the lowest of the soot cases. However, even though the soot mode for this case is small, both direct measurements and optical properties indicate that soot absorption is present (see section 3.8 below). As a

result of these observations we have also indicated a so-called "reference" dust distribution for the high dust case that decreases rapidly at OES below 0.5 μm. The difference between this "reference" dust distribution and the measured refractory accumulation is taken to represent the refractory soot and BC component. This approach assumes that the refractory soot is confined to sizes below 0.75 μm and that none resides on the surface of the dust mode. However, we will demonstrate that this assumption is not always true later in the paper.

The bottom panel in Figure 5 shows the normalized refractory OES for the 250 m leg along with the reference dust distribution (RefDust). The refractory soot component is obtained by subtracting the normalized RefDust from the total refractory distribution. Several lognormal modes are illustrated as number distributions along with the lognormal fit parameters (Table 1) that are used to describe the refractory distributions. The smallest sub-μ mode describes the variability of the soot/BC aerosol. Although the dust mode appears monomodal it requires three lognormal modes to fit it for all conditions. The dust mode centered at about 0.8 μm is common to both elevated and lower dust concentrations reflecting a lack of sensitivity to variations in production and removal processes. The larger dust mode reveals the more variability in dust concentrations at diameters near and above 2 μm. These two modes encompass those sizes contributing most to dust optical properties at visible wavelengths. A third lognormal mode is needed to describe the largest dust behavior but is not included here since this varies significantly and it is poorly characterized by our instrumentation due in inlet efficiency and counting statistics.. The larger modes here have unusually high concentrations for this major dust event and all modes need to be scaled to represent concentrations appropriate for a given distribution. The steep fall off in RefDust volume on this log-log plot below about 1 μm and the more gradual increase to a maximum near 10 μm is consistent with results of size-resolved elemental analysis of dust samples from the Negev desert (Maenhaut et al., 1999) and from the Sahara (Schütz, 1980). The equation describing the sum of the second and third lognormal fits to the 250m leg in terms of the parameters in Table 1 is:

Eqn. 1. $$\frac{dN}{d \log D_p} = \sum_2^3 \frac{N_i}{\sqrt{2\pi} \log \sigma_i} \exp\left(-\frac{(\log D_p - \log D_{pi})^2}{2\log^2 \sigma_i}\right)$$

Table 1. Lognormal fit parameters to the number distribution in Figure 5c. N_i is the concentration, D_{pi} is the geometric mean or median diameter and σ_i is the geometric standard deviation as defined in Seinfeld and Pandis (1998).

	1	2	3
N_i	480	30	39
D_{pi}	0.12	0.75	1.65
σ_i	1.73	1.35	1.82

3.4   Absorption and Refractory Aerosol

Since BC does not break down in air until heated above 700°C (Smith and O'Dowd, 1996) this refractory material must include the refractory light-absorbing BC. Other possible components of the refractory soot aerosol include non-absorbing (or relatively low absorbing) organic carbon (OC) remaining at over 300°C (Mayol-Bracero, 2002) and possible fly ash. Hence, the OPC refractory volume below 0.75 μm should be closely related to the light absorption coefficient. Figure 6 shows this refractory component as measured every 90 sec plotted against the total measured PSAP absorption coefficient for both TRACE-P and ACE-Asia experiments. The ACE-Asia data has refractory volume corrected for the measured dust component based upon the scaled reference dust distribution discussed above. Fewer data points are evident on TRACE-P because the PSAP measurements of absorption were cycled between total and sub-μ (aerodynamic) sizes on TRACE-P while two PSAP instruments provided continuous data on ACE-Asia. This cycling required for TRACE-P also introduces some intrinsic scatter in TRACE-P absorption data because measurements are sequential and not coincident in time. Even so, this refractory mode is closely related to absorption in TRACE-P with an R^2 of 0.94. This shows that absorbing BC is a significant fraction of the refractory aerosol and related studies in the Indian Ocean Experiment (INDOEX) suggest nearly half of the mass in this mode was BC (Mayol-Bracero et al., 2002).

The ACE-Asia data show a similar strong dependency, indicating that for most data with exceptions above and below the indicated line (discussed next). A strong relationship with a slope similar to TRACE-P also exists for ACE-Asia but there are groups of data that cluster above this slope and also below this slope. Both the dominant groupings for relative absorption (around line- 68% of data points) and the higher (above line, 17%) and lower (below line, 15%) are linked to characteristics of the aerosol size distributions and optical properties. The data points above the TRACE-P regression line indicate less absorption for the measured sub-μ refractory volume. These cases were primarily in and downwind of the Yellow sea and reveal a low absorbing refractory component unrelated to dust. These properties are consistent with SiO_2 spheres produced by some low temperature coal combustion in the region (T. Cahill, personal communication) (J. Anderson et al., 1996) but may also include enhanced sub-μ flyash or refractory OC. Those cases to the right of the line reveal the role of coarse dust absorption as indicated for high dust when coarse volumes exceed 200 μm^3 cm^{-3} (solid black dots).

3.5 State of mixing in the accumulation mode and smaller sizes.

Here we return to the role of volatile aerosol components associated with the refractory aerosol discussed above. As mentioned in the introduction, the state of mixing of the aerosol can often be inferred from the volatility. If the mass changes but the integral number do not then the volatile component must be internally mixed with the refractory component. If both number and mass change then some or all particles may be externally mixed depending upon the change in the size distribution. Hence, it is important to have measurements from both the OPC (Fig. 4) and DMA in order to resolve changes in both volume and number over the size ranges of interest.   Figure 7 shows both DMA size distributions at 40°C and 350°C including associated TDMA data

for two TRACE vertical profiles. One is for a profile flown out of Yokota Japan and the other out of Hong Kong. The middle panel shows vertical profiles of the ratio of CH_3Cl to C_2Cl_4 for both profiles as an indicator of the relative influence of biomass burning. Values near the surface in both profiles are lower and more indicative of urban sources while both increase aloft with the greatest increase over Hong Kong indicative of a more pronounced biomass burning in that region. These features are consistent with the similarities in average near-surface ϖ values and their differences aloft for data north and south of 25°N, as shown in Figure 3. Thermal DMA distributions are shown on either side of the central plot with arrows pointing to where the distributions were measured. Above 4 km concentrations are lowest and indicative of less polluted air with limited influence of biomass aerosol. Much higher concentrations are present below that altitude for both profiles. A brief description of each case follows.

A)   At 4.3 km over Yokota, Japan, a monomodal unheated peak with little change on heating to 150°C suggests mostly neutralized sulfate coating aerosol is common (Clarke, 1991). The broadening of the refractory mode to smaller sizes after heating suggests smaller aerosol may have a relatively greater volatile coating while larger have less volatile coating. This is consistent with condensational growth of refractory primary particles from a variety of sources. .

B)   At 1 km over Yokota, Japan. Larger change on heating to 150°C suggests only partial neutralization of sulfate aerosol (or possibly ammonium nitrate) present in larger 0.1 μm sizes while separate smaller mode near 0.03 μm is nearly completely volatile, consistent with recently nucleated sulfuric acid. Refractory distribution at 350°C has same number as 150°C distribution but about a factor of 3 smaller indicating only about 5% of the mass remains. This implies a refractory soot component is internally mixed with about 95% of volatile mass.

C)   At 0.3 km over Yokota, Japan. This is similar to above only with no smaller volatile nuclei mode. More refractory mass remains at sizes near 0.1 μm.

D)   At 4.3 km over Hong Kong the heated distributions are at low concentration and appear bimodal with one peak near 0.04 μm merged with another near 0.1 μm. At 150°C the larger mode shifts slightly smaller indicating probable neutralization (similar to ammonium bisulfate) but the smaller mode shifts more indicating larger sulfuric acid fraction in this mode. At 350°C the larger mode appears to be completely volatile, as commonly observed for a naturally formed aerosol in the free troposphere (Clarke and Kapustin, 2002), while refractory particles appear to remain in the smaller mode after driving of the volatile component. This is a relatively unusual case that suggests an aged volatile FT aerosol (larger mode) has been mixed with small refractory nuclei associated with combustion (smaller mode) that may have been scavenged by cloud in the larger sizes. Other possibilities include volatile organics in the larger sizes also observed in biomass plumes (Posfai et al., 2002).

E)   At 3 km over Hong Kong a moderately high concentration looks like a typical aged biomass aerosol plume. At 150°C it shifts appreciably to smaller sizes indicating a significant sulfuric acid fraction that has not been neutralized. At 350°C it shifts a little more but preserves a clear mono-modal shape with a significant number remaining at larger sizes above 0.1 μm. This refractory BC mode shows less change in diameter upon volatilization and with fewer particles at smaller sizes than the more urban

distributions. Number is not conserved upon heating and indicates externally mixed volatile aerosol.

F) At 0.3 km over Hong Kong the distribution is similar to the near surface distribution seen over Japan (C) and with a relatively larger shift upon heating compared to the biomass plume above (E).

The discussion above is based upon apparent changes in the overall DMA distributions but is confirmed when TandemDMA (TDMA) heated scans are done on specific size classes. A few of these are shown at the bottom of the panel for sizes selected from cases B, C and E. The size class selected near 0.1 μm in case C has a peak shift to near 0.035um upon heating to 350°C with only about 7% remaining near the original size. This subgroup may be externally mixed or associated with little volatile material while the other 93% of the particles in this size class are associated with significant volatile material. A similar selected size for case B near 1km altitude shows less than 1% of the total number remains in the selected size range after heating, indicating that all are internally mixed in this size class. However, the sizes selected at 0.04 μm are completely volatile upon heating to 350°C confirming our impression above for the behavior of this mode. Hence, this smaller mode is consistent with volatile particles formed from homogeneous nucleation in the gas phase while the larger mode is formed from heterogeneous condensation on the refractory soot and BC aerosol. A simlar selected size from the biomass plume (case E) also shows a volatile aerosol with a refractory component but with a much smaller spread in diameters upon heating than for the urban pollution cases. Again this is consistent with our interpretation of the original full DMA distribution. It is possible that a few particles near the original size may have been externally mixed but these would be less than 5%.

These observations are representative of many others and confirm that the aerosol is usually internal mixtures in the accumulation mode. Flight legs below 2km altitude encompassed most of the high aerosol cases during TRACE-P and ACE-Asia and the accumulation mode had a refractory residual soot component that was internally mixed, as shown above. The aerosol number concentration was typically dominated by primary combustion- derived particles and not by nucleation of new particles. However, occasionally the nuclei mode aerosol was completely volatile, particularly for low altitude cases in and downwind of the Yellow Sea. These were often related to recent nucleation followed both by rapid growth and coagulation during the day (McNaughton et al., 2003) and attributed to condensation of sulfuric acid (Weber et al., 2003). We have assumed sulfuric acid condensation in the discussion above for simplicity but other vapors including OC are certainly involved since the ratio of organic carbon to sulfate in the ACE-Asia aerosol was often near one (Bertram et al., 2003). Such condensation should occur on all surfaces and contribute to the observed volatility in the accumulation mode as well as adding volatile material to the coarse aerosol.

Some differences are evident in the TDMA data for case C and E. The TDMA case C also shows about 7% of the number retain their original size, indicating that these may be externally mixed. The TDMA case E (biomass example) shows a shift in size that preserves a nearly monomodal shape compared to the urban case C that shows a broader distribution after heating that is skewed to smaller sizes. The general shift to smaller sizes is also evident in the associated full DMA distributions. Similar differences have

been evident in our data for biomass vs. urban measurements of refractory (BC) distributions measured over the Indian Ocean and off the coast of South America, suggesting that this may be characteristic differences in these types of combustion sources. This indication of a larger and narrower soot/BC population in biomass plumes compared to a broader distribution in urban plumes may reflect the multiplicity of diverse combustion sources in the latter.

3.6   Comparison of volatile aerosol components and PILS soluble species

In spite of the complexity of the Asian aerosol we were able to compare the volatility in sizes larger than 0.1 μm, as evident from the OPC (Figure 3, lower middle panel), to the PILS technique for rapid in-flight measurements of soluble ions. The PILS employs a steam saturator to grow the aerosol to sizes that result in liquid impaction followed by measurement of major ions every few minutes using ion chromatography. The PILS configuration for these experiments sampled only those particles with sizes below about 1.3 μm aerodynamic cut size (Orsini et al., 2003). In order to compare soluble and volatile species we first had to adjust our optically effective OPC sizes to geometric sizes in order to estimate associated mass. In order to do this we first estimated the refractive index of the actual aerosol sampled by the OPC and correct for sizing based upon the reference refractive index of 1.588-0.0i. The actual refractive index is estimated from the refractive index of the refractory soot component mixed with species volatile at 350°C and assumed to have the same refractive index as that for sulfate. These calculations also assume the refractory soot was about 40% BC, 40% refractory OC and 20% dust by volume that was internally mixed with volume weighted refractive indices.

The size at the new refractive index is determined when it yields the same calculated scattering detected by the OPC (which resulted in the original OES measured by the OPC). Because the PILS instrument removed larger particles, the OPC data was integrated only over those sizes that would have been measured by the PILS, as determined by the transmission efficiency curve in Figure 8. As an illustration of the result of this process both the OES from the OPC and the recalculated geometric sizes expected after the size cut are shown in Figure 8 for OPC data at all three temperatures. The actual mixture is more complex and more difficult to model (see discussion section below) but for this approach the resulting sub-μ adjusted volume for this example is about 15% less than the original unheated OES volume.

Once size-adjusted in this fashion then the refractory volume can be converted to mass based upon an estimated soot density that includes BC and refractory OC. Though hard to quantify, we have used an effective density of about 1 g cm^{-3} for OC and 1.9 g cm^{-3} for BC but recognize that variations about this value may be expected. This insoluble component can then be added to the measured PILS soluble species to get the total soluble and insoluble mass. This is shown in Figure 8 for all of TRACE-P flight 5 and the resulting total mass is compared to the adjusted OPC total mass. The agreement is quite good with the combined refractory mass and PILS soluble components accounting for 85% or so of the total estimated OPC mass. This difference of 15-20% could reflect both uncertainties in the model approach and/or unanalyzed species expected to be present such as OC. The latter exhibited similar average concentrations to

sulfate during ACE-Asia (Bertram et al., 2003) and would be consistent with this difference. Hence, this close agreement over an order of magnitude variation in concentrations and diverse altitudes suggests that this basic physiochemical description of the aerosol is reasonable. The relationship between volatile and soluble aerosol species improves our ability to use volatility to infer characteristic aerosol chemistry, optical properties and humidity dependent growth.

3.7   Refractory Soot, BC and EC relationships

The data presented above examined links between BC absorption and the size distribution. Other measurements of elemental carbon, EC, based upon CO_2 evolved from heated samples are also used to assess the mass of carbon present. A variety of techniques are used which differ in their approach and the manner in which EC is operationally defined (Huebert et al., 2001, Lim et al., 2003) but ACE-Asia employs the approach developed by Sunset labs. (Bertram et al., this issue) having an estimated uncertainty of 30%. The sampling times for EC on the C-130 was generally on the order of 30 min. because appreciable sample is required to increase signal to noise. Hence, only leg average values are available for comparison. These leg average regressions between BC absorption, refractory volume and EC are shown for the ACE-Asia data in Figure 9 for data below 2km. Four anomalously large values for EC were removed because they were not evident either in BC absorption or refractory volumes. Plots include both sub-μ and total measured PSAP absorption. EC is related to absorption with an R^2 of about 0.24 for both total and sub-μ plots. Uncertainty arises both through many measurements being near detection limits and the operational definition of EC including the correction for charring of OC to BC (Bertram et al., this issue).

This uncertainty impacts the interpretation of the zero value of derived EC (so-called EC/OC split) and thereby the intercept for zero absorption in Figure 9. Although the two indicated regressions for total and sub-μ absorption yield an MAE of 6 and 9.5 $m^2\,g^{-1}$ the large scatter in the data include many other values that range from about 3 to 12 $m^2 g^{-1}$. Moreover, the observed presence of larger BC aerosol with low MAE values but significant mass would tend to lower overall MAE value obtained from the EC measurement approach and could result in some of the relatively low absorption cases in figure 9. Hence, if we exclude several of the highest EC values for values of PSAP absorption below about 6 Mm^{-1} (ie. lowest MAE values) and also assume that sub-μ absorption is due to the BC component then most remaining MAE data lie between about 5-10 $m^2 g^{-1}$.

The plot of sub-μ refractory volume against EC in Figure 9b has an R^2 value of about 0.32. Some of the outlier points can be excluded for reasons of inconsistency between EC, BC and refractory volume but the mean slope remains similar to the indicated solid line. This relationship indicates that OES sub-μ volume cannot be pure BC with an estimated density of about 1.9 $g\,cm^{-3}$ (FMK). The two dashed lines represent the predicted relation between refractory volume and EC(BC) assuming the BC is either 60% or 100% of refractory volume. Although it may be possible that refractory volume is 100% "pure" BC (here we assume the refractive index of 1.95-0.66i) the thermal analysis for other Asian aerosol (INDOEX; Mayol-Bracero, 2002) suggest that the refractory OC mass evolved at temperatures above 300°C is generally about 60% ± 20% of the BC mass. Little other refractory mass was reported by these authors. Consequently, the dashed lines reflect BC fractions of the refractory component that

range between most typical INDOEX data (60%) and the potential for all refractory aerosol to be 100% BC. Although the EC measurements have significant uncertainty (Bertram et al., this issue) the regression suggests that the BC fraction of refractory volume varies around 70% of the total refractory volume. However, because some EC is certainly in sizes larger than the sub-μ refractory OES volume (see Section 3.9), lower BC percentages will be more representative the sub-μ aerosol.

Figure 9c shows leg averaged examples of the data shown in Figure 6. It shows that sub-μ refractory OES volume is more closely linked to sub-μ BC absorption than EC with an R^2 of about 0.74. Values for total absorption are also plotted but have a lower R^2 of 0.64. This indicates that absorption by coarse particles is generally less than sub-μ absorption but can account for at least 10% variance in total absorption over the ACE-Asia mission. When converting sub-μ OEV to estimated BC mass we have to allow for refractory mixtures of BC, refractory OC and possibly other refractory species remaining at 300°C. Here we assume likely densities for BC of about 1.9 g cm^{-3} (FMK et al., 1999) and OC of about 1 g cm^{-3}.

Adjustments for the OPC sizing are also needed for highly absorbing aerosol (Pinnick et al., 2000). We have measured an oversizing by the OPC for carbon aerosol of about 8% for diameters below about 0.4 μm (Clarke, 1991) such that actual sub-μ refractory volumes are estimated at about 80% of measured OEV volumes (V_{sub}). The total OC mass (or Particulate Organic Matter – POM) has been related to the measured OC carbon evolved in EC analysis for ACE-Asia by a multiplier of about 1.4 (L. Russell, personal communication). We apply this value to the to the refractory OC mass to get refractory POM. Refractory mass is the sum of BC mass and refractory POM. Actual refractory volume is the sum of BC volume and POM volume obtained by dividing these masses by their respective densities. Hence, after applying these relations and densities we can use the range of values above for BC to refractory OC obtained for INDOEX to obtain an expression for BC mass (measured in μg m^{-3}) equal to about 0.6 ± 0.15 times our measured OEV values (measured in μm^{-3} cm^3). Hence, the plot in Figure 9c has a slope equal to the OPC volume absorption efficiency (VAE) that can be converted to an effective MAE for BC of about 8.5 ± 2.5 m^{2}g^{-1}.

Higher MAE values for BC would be obtained if smaller fractions of BC were present in the refractory component but this would be inconsistent with most INDOEX data. TRACE-P is expected to be similar to INDOEX data in character and sources. Because TRACE data also has a similar relation between PSAP absorption and refractory volume as most of the ACE-Asia data (Figure 6), it is expected that this range of values is representative of these data sets. This MAE estimate is also consistent with most values of EC and refractory volume shown in Figure 9b. In any event, the relationship of BC with refractory OEV is much stronger than between BC and EC and supports our use of refractory volume for assessing the optical properties of the soot/BC combinations. However, before we focus further upon BC absorption it is helpful to consider the high dust cases so that the optical properties of dust can be determined and extracted from our consideration soot/BC optical properties.

3.8   Determination of the Refractive Index for Asian Dust from Flight 13

We determine the refractive index for the Asian dust by finding the real and imaginary components that provide consistency between measured and calculated scattering, absorption and ϖ both the total and sub-μ OPC size ranges. Because we need

to be able to extract the dust size distribution from the total we focus first on dust by analyzing observations during the heaviest dust case encountered during ACE-Asia Flight 13 in the Yellow Sea. This allows us to explore the limiting behavior for dust absorption but does increase uncertainty in the extraction of the soot component from the sub-µ refractory mode. The data between 3:00PM and 7:00 PM (Figure 10) include a vertical ascent followed by a stepped descent with stacked alternating north-south legs at 5,500 m, 700 m and 250 m. Marked horizontal and vertical variability is present but highest dust and pollution concentrations are present near the surface and generally toward the center of each leg. The volatility data (Figure 5) reveals a low soot component for the leg near 5.5 km but increasing soot fractions upon descent, as is also evident in the absorption values in Figure 10. Consequently, we use these cases to explore and constrain the real and complex refractive indices for the absorbing dust and soot components.

   The heated and unheated size distributions during this period (eg. Figure 4) indicate that most particle volume is refractory dust with some volatile particles in the accumulation mode. Dust was also evident in large concentrations of calcium in the PILS measurement. If we assume that dust is the dominant particle absorber for this case then the complex refractive index for the size distribution that generates the observed absorption will be the maximum value dust can have. The presence of other higher absorbers (eg. BC) would mean that contributions from dust absorption would be even less. In general, in order to establish diameters for Mie calculations the OES diameters from the OPC have to be adjusted to account for the difference in refractive indices between the calibration glass beads and the actual particles. However, because calibration beads have refractive indices of 1.588 and 1.54 for larger sizes they are close to dust real refractive indices and changes in calculated scattering for these differences are less than 1%. This approach assumes that the influence of a small amount of absorption on OPC derived scattering is negligible. For the absorption considered here this was calculated to be less than 5%. Hence, the OPC effective OES diameters of the dust as measured can be used directly for the Mie calculations. The imaginary part of refractive index of dust is low but allowed to vary from 0.0003 to 0.0052, while the real part was fixed to 1.53 [Woodward, 2001]. As mentioned earlier, the actual size of volume equivalent spheres are likely to be smaller since irregularly shaped particles scatter more than equivalent spheres (Koepke and Hess, 1988; Mishchenko et al., 1997; Kalashnikova and Sokolik, 2002). However, at this point we are interested in measured and modeled optical properties so it is only the measured OES that concerns us.

   Confirmation that scattering calculated from OES sizes agrees with the measured scattering is based upon comparison of both values calculated over angles between 7°-170°, as measured by the nephelometer. This avoids the ambiguity in any error in the truncation correction for the nephelometer when particles sizes are very large (Anderson et al, 1996). However, the scattering angle of the OPC is only 35° to 145° and our OES sizes assume similar scattering between OES spheres and ambient aerosol outside that angular rangebut this influence is expected to be relatively small. The next step is to include a complex refractive index to generate an absorption coefficient for the dust consistent with that measured by the PSAP. However, because low absorbing aerosol have a maximum in their MAE values at larger supermicrometer sizes compared to BC (see below) we need to be aware of transmission losses for larger particles in the PSAP.

We have measured this as a function of OPC effective optical size using our archived El Chichon volcanic dust and the size dependent transmission for the PSAP as a function of low rate (not shown) and determined that at 1 lpm it had a transmission of 50% at 12.5 μm and 80% at 7 μm OES. This leads to a small correction for absorption on ACE-Asia at highest dust loadings. A volumetric flow rate on ACE-Asia was about 1 lpm and on TRACE-P was about 4 lpm requiring different size dependent corrections for each data set. Fortunately, the TRACE-P experiment encountered little dust so these corrections were negligible with isolated exceptions.

Application of the above approach is focused upon the 700 m leg because it has high dust absorption associated with low to moderate absorption due to BC (Figure 5). The best fit to the coarse mode absorption and scattering was found with an effective refractive index for dust of n = 1.53 - 0.0005i (±0.0001i). This was established as an effective refractive index for spherical particles that scatter the same as the measured dust. However, for these particle sizes the difference between spherical and nonsperical absorption cross sections are calculated to be only about 2% (Mishchenko et al.,1997) implying that this refractive index applies equally well to the irregular dust aerosol. Values for the BC absorbing component are discussed separately below. These values also provided a good fit to total scattering except for overestimates during the highest scattering values during ACE-Asia. This is expected to be most uncertain due when the steep impactor size cut overlaps a steep increase in dust volume. As dust concentrations drop to values more characteristic of ACE-Asia (e.g. periods of lowest scattering values for the 3 legs shown in Figure 10a) the agreement is excellent. Agreement is also excellent for total and sub-μ absorption (Figure 10b) during these periods. However, the underestimate of sub-μ absorption increases to about 30% where dust concentrations are highest. This is almost certainly due to the sensitivity of sub-μ absorption (refractory soot volume) to the subtraction of the refractory dust tail at highest dust loadings and/or complications arising from BC attached to dust in the vicinity of the cut point that are not modeled here but are discussed below.

Figure 10c shows measured and modeled total and sub-μ values for ϖ during these legs. The OPC-derived ϖ is the OPC-derived absorption divided by the sum of the OPC-derived absorption and the scattering retrieved from the OPC distributions using the calibration refractive index of 1.588. The measured ϖ is the adjusted PSAP absorption divided by the sum of the adjusted PSAP absorption and the scattering measured by the nephelometer at 550 nm. The best agreement is again evident for the moderate dust concentrations characteristic of ACE-Asia but poorer agreement, particularly for sub-μ ϖ, is evident in the highest dust periods.   The better overall agreement at moderate dust concentrations suggests that the BC refractive indices used are reasonable and that the approach should yield good results for these lower dust concentrations. Apart from sensitivity to the dust subtraction approach some of the disagreement at highest dust concentrations is because the dust model does not account absorption due to the incorporation of soot onto dust that can be enhanced in high dust events.

3.9 Soot Incorporated onto Dust

A related issue of interest is the interaction of pollution aerosol with dust and possible influences on aerosol optical properties.   When this occurs through coagulation at typical

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ambient humidity or though in-cloud collection processes the net effect is to transfer smaller aerosol, including BC, to the surface of larger aerosol to create enhanced apparent absorption by larger aerosol relative to those without BC on their surface. While this may have an uncertain influence the net MAE of BC it can affect the residence time of BC as well as the inference of coarse dust optical properties obtained from collected samples. Scanning electron microscope (SEM) images confirm soot and BC can be present on Asian dust (Figure 11). These examples are again from Flight 13 of ACE-Asia in the Yellow Sea at altitudes of 5,500 m, 700 m and 250 m. The high altitude sample shows generally sharp edged dust aerosol with some occasional soot particles but the size of soot clusters, their abundance and attachment to dust surfaces increases at low altitudes. Most isolated soot clusters and round "balls" have a graphitic nature and were originally coated with volatiles (open circles). Note that thermal heating of the particles by the high beam current in the SEM during this analysis drives off many volatile species such as sulfate and OC (Posfai et al., 2002) leaving the more refractory components shown here. We presume those BC particles remaining in these images are similar to those detected in the 300°C OPC OES distributions.

These images clearly confirm that soot can be attached to the dust surface but it is difficult to develop statistical assessments of the state of mixing or consequences for optical properties. They also point out the difficulty in assigning shapes or volumes to these irregular particles but do suggest that their aerodynamic and optical behaviors are likely to be quite different from mass equivalent spheres. This causes considerable uncertainty in taking such data and modeling particle optical properties. However, because our OPC distributions are based upon the optically effective scattering of each particle it provides OES sizes that can be directly modeled as equivalent Mie scattering spheres. Hence, we will explore the optical impact of soot on dust (and coarse particle soot) by comparing coarse particle absorption with coarse particle optically effective volume (OEV) obtained assuming spheres with OES diameters.

We have stratified size distributions into OES diameters larger than the 0.75 μm (ca. 1.0 μm aerodynamic) for comparison to coarse particle absorption obtained from the difference between PSAP total and sub-μ light absorption measurements (Masonis et al., 2003). We define elevated dust concentrations when coarse particle volumes exceed about 200 $\mu m^3 cm^{-3}$. These cases exhibit significant coarse absorption, as implied in ACE-Asia data (Figure 6) where total absorption deviates to the right of the "signature" line for soot/BC absorption. However, because we want to evaluate the observed coarse particle absorption per unit mass, as detected by the PSAP,we have corrected the OEV distribution to reflect the PSAP transmission efficiency. Because the OPC measures the OEV of the aerosol it is convenient to examine the associated particle absorption per unit volume or volume absorption efficiency (VAE) before converting results to the more familiar MAE. The measured coarse particle absorption per unit coarse particle volume OEV is shown in Figure 12a vs. the coarse OPC particle volume for all ACE-Asia data and with data from flight 13 highlighted. Large variability in coarse volume below about 100 $\mu m^3 cm^{-3}$ is primarily due to uncertainty in the coarse absorption obtained from the difference of total and sub-μ absorption. This can be within the PSAP noise limit for short sample periods when coarse absorption is low. At higher coarse volumes the VAE values approach an asymptote near 0.018 Mm^{-1} μm^{-3} cm^{-3} but tend to considerably higher values as volumes decrease.

We expect that the enhanced scattering of non-spherical particles result in OEV's larger than actual volumes. Estimates of this effect for the angular range detected by the OPC vary from about 1.3 [Kalashnikova and Sokolic, 2002] to 2 or so [Koepke and Hess, 1988]. Hence, to

estimate MAE from VAE we must increase it by an estimated 1.7 ± 0.4 to convert our OEV to actual volume. At the same time, in order to convert from volume to mass we must also divide VAE by about 2.5 g cm^{-3} assumed here for the dust density. Application of these values to the VAE in Figure 12b means that the data asymptote to an equivalent sphere MAE value about 0.66 times the indicated VAE value only with units of m^{2}g^{-1} and with an uncertainty estimated near 30%. Highlighted data are from ACE-Asia flight 13. The 700m leg (red dots) had high dust concentrations with relatively low BC concentrations (see Fig. 5) and suggest an asymptote for MAE equivalent to about 0.012 ± 0.003 m^{2}g^{-3}.

    As soot concentrations in the 250 m leg were about 4 times higher than the 700 m leg, the higher VAE at 250 m (green dots) is probably due to soot attached to the dust. There were no observed mineralogical differences. The more commonly observed dust concentrations evident below about 300 μm^3 cm^{-3} (OEV) show VAE values elevated by factors of 2 to 5 above the asymptotic dust value for many of these measurements. This also suggests the presence of absorbing BC on the dust surface for these cases. However, the size dependence of MAE for dust and the consequences of the impactor size cut need to be included before this behavior can be properly interpreted (see Discussion below).

4.   Discussion

        The data presented above provides a means to quantify our understanding of the physical, chemical and optical properties of the aerosol in terms of characteristics of the size distribution. It was demonstrated that the accumulation mode is predominately internally mixed with a refractory soot component often dominated by absorbing BC. We also resolved the characteristic shape of the optically effective dust component allowing us to estimate and remove its contribution to sub-μ aerosol refractory volume so as to better determine the refractory soot-only volume. The ambient volatile aerosol component was also linked to measured soluble ions allowing us to refine size dependent properties of the refractive index and related water uptake, important for modeling aerosol growth in response to changes in ambient RH. These considerations allow us to make assessments of how size-resolved scattering and absorption provide constraints on aerosol intensive properties such as effective real and complex refractive indices and the size resolved mass scattering efficiency (MSE) and mass absorption efficiency (MAE) of dust and soot.

4.2   Refractory Size Distributions and Absorption: Soot and Dust Optical Properties

    Figure 13 illustrates the effect of size and compositions on optical properties of spherical particles. Here we employ the OES refractive index 1.53 –0.0005i as determined above (Figure 13) and a BC refractive index of 1.95 – 0.66i representative of diesel soot (FMK; Bergstrom, 1972). Lower values are possible for other soot and would lead to correspondingly lower MAE values. The complex refractive index of soot mixtures (BC + refractory OC + etc.) will also be lower depending upon the fraction of absorbing BC they contain. Figure 13a shows that Mie calculations for pure BC diameters below 0.2 μm the MAE approaches a constant near 4 m^{2}g^{-1}. However, little BC mass is generally found below 0.1 μm (Figs. 4 and 8). If BC has the same size

distribution as the refractory aerosol sizes after correction for absorption (Sect. 3.7) then the integral effective MAE is calculated at 4.7 m^2g^{-1}. Sizes near 0.2 μm show a peak in MAE near 6 m^2g^{-1} butMAE values continually drop with an inverse dependence on size above about 0.3 μm due to incident light being absorbed in the surface layer of the BC particles while the shielded mass toward the center does not contribute to absorption. Thus the large EC "balls" shown in Figure 11 contribute fully to EC mass measurements but have low relative BC absorption. Although they are not common 5 μm balls in Figure 11 have the volume of about 5,000 BC particles of 0.3 μm diameter but an MAE of only one tenth their value.

Furthermore, if soot (BC and refractory OC) is internally mixed with sulfates and OC etc. the absorbing properties of the mix measured by the PSAP may be larger than that of pure BC. BC stuck on the surface of sulfate is estimated to only increase the MAE of BC by about 15% while if mixed internally it may increase MAE values much more (FMK). These calculations are for dry collected aerosol and not the hydrated mix expected in the ACE-Asia boundary layer. Examples of both morphologies are suggested by SEM observations of dry BC/sulfate mixes on ACE-Asia particles but the surface attachment appears common here (J. Anderson, personal correspondence) and in remote regions (Posfai et al., 1999). Internal mixes appear more common in biomass plumes (Posfai et al., 2002). Because the BC component is probably hydrophobic it may reside primarily on the surface of a wet aerosol or one processed through cloud.

However, given the small BC fraction of the sub-μ aerosol it is likely that the BC can also be encapsulated and mixed with some OC and sulfate etc. When this occurs, and depending upon the size and mixing state etc., it is predicted to raise the MAE of BC as much as a factor of 2 or more over BC alone (FMK). This has been confirmed in recent carefully controlled coating of nearly monodisperse 0.24 μm diesel soot with α-pinene. Stepwise growth in a chamber over a 12 hour period increased particle volume by about a factor of 3 and absorption by a factor of two (Saathoff et al., 2002). Evidence in our data for this effect is shown in Figure 14a where we plot the sub-μ VAE for the refractory volume vs. the ratio of volatile to refractory sub-μ components. The VAE increases as this ratio increases and the slope suggests that the absorption of the BC is enhanced by this condensed matrix but by about a factor of 1.5 for about a 3fold increase in average volatile volume. Because both axes share the same denominator they are not independent but this behavior is consistent with the expected amplification of BC absorption by condensates. A similar plot in Figure 14b shows the same effect where the volatile volume has been replaced with the sum of OC and non-sea-salt sulfate. This is also similar to a plot showing the increase in MAE of EC with the latter (Bertram et al., this issue). Hence, our modeled absorption for externally mixed BC is expected to underestimate the effective BC absorption. In both plots the VAE intercept is near 3 Mm^{-1} $μm^{-3}cm^{-3}$ at the limit of no volatile components. We note that if the relation of BC to OEV used above (Sect. 3.7) is applied then this apparent intercept corresponds to an MAE of 5 m^2g^{-1}, close to our theoretical estimate for pure BC with for this size distribution. Similar scaling of the overall data shows that our previous estimate of an effective MAE of 8.5 ± 3 m^2g^{-1} for the mixtures (Sect. 3.7) captures the average values and most of the variability evident here, although about 20% of the data in Figure 14 exceed 11.5 m^2g^{-1}.

Another issue is evident when looking at the morphology of soot/BC particles such as those shown in Figure 11. Some isolated soot/BC particles are present in the 0.1 to 0.2 μm range but larger soot/BC particles are often made up of aggregates of these primary sphere sizes. This makes interpretation of the MAE plot for BC in Figure 13a problematic since it assumes spherical particles at each diameter. As mentioned earlier, the fall off in MAE for sizes above about 0.3μm is due to the surface absorption of light that effectively excludes the center from contributing to absorption. However, if 0.4 μm particles are comprised of say eight 0.2 μm primary BC particles (and some OC etc.) it is unlikely to have the indicated MAE of about 2.5 m^2g^{-1} since calculations for up to 10 primary spheres of 0.1 μm diameter show small changes in MAE on aggregation (FMK). This suggests that effective MAE values for BC aggregates larger than 0.2 μm may be nearer values shown for 0.2μm particles in Figure13a. Addition of a refractory BC "resin" non-absorbing coating of 33% by mass also appears to increase MAE of say 20% over the values shown for pure BC in Figure 13a (FMK). Hence, the MAE values in Figure 13a may apply best for the single particle spherical soot/BC evident in Figure 11 but would need to be increased for the aggregated soot/BC particles larger than about 0.2 μm. However, calculations of MAE for aggregates of BC with associated refractory OC are complex and must also allow for shadowing effects.

These issues impact the conversion of our effective OES distributions from the OPC when we want to convert measured OEV to actual volumes (and actual mass) because high absorbing aerosol also affects sizing by the OPC (Pinnick et al., 2000). This is complicated by their results that show sizes of BC below 0.32 μm to be oversized (more scattering) by the OPC while those larger will be undersized relative to our calibration aerosol. To some extent this may have compensating effects on total volume because 0.32 μm (size where no effect on OPC sizing is expected) is near the peak in the refractory soot/BC mode volume (see Figures 4 and 5). However, the Pinnick et al. analysis does not address the aggregation effects discussed in the previous paragraph so their analysis for particles larger than say 0.2 μm would need to be modified for this kind of aerosol. As mentioned earlier (section 3.7), an empirical evaluation of sizes for absorbing aerosol revealed about 8% oversizing by the OPC for sizes up to 0.4 μm (Clarke, 1991). This yields actual volumes about 80% of OEV values and we assume these results apply here. We also note that the simple mixing rule assumption (implies a soluble well mixed BC) initially made in section 3.6 for the PILS analysis is therefore inappropriate. Even so, the estimated actual volume from that assessment for this size range resulted in a similar net reduction in refractory OEV volume of about 15-20%.

Figure 13b illustrates the calculated size dependent values of ϖ for the typical dust, soot (refractory) and mixtures of soot and soluble species using the refractive indices described above. These are taken as representative of the TRACE-P and ACE-Asia aerosol. The sub-μ values of ϖ for the dust component are essentially 1 but drop to about 0.9 for OES diameters near 6 μm. Hence, the appropriate MAE value for dust depends on the dust size distribution. Results are also shown for arepresentative mixture of BC and volatiles etc. (74% volatile, 8%BC, 8% refractory OC, 8%dust) in the sub-μ accumulation mode. Values of ϖ for sizes between 0.15 and 0.75 μm are seen to range from about 0.6 to 0.8 depending upon variations in the effective volume (mass) mean diameters for this mode (commonly between 0.2 and 0.5μm). Again, these are modeled

here as external mixes and if the BC enhancement discussed above is applied the values of ϖ will lower accordingly.

The comparison of measured and calculated optical properties is extended to the entire ACE-Asia data set in Figure 15. Here again an external mix is assumed in the calculations. The ACE-Asia data set is shown since it includes the more variable aerosol mixes evident in Figure 6. Here we compare calculated values to the scattering coefficient and absorption coefficient "seen" by the nephelometer and PSAP respectively. This means that optical properties modeled from size distributions have been designed to correspond to angular scattering present in the nephelometer and have been adjusted to allow for aerosol transmission losses in the PSAP. The Flight 13 data is highlighted in color and superimposed upon the full data set shown in grey. These are further broken down into total, sub-µ and coarse values for each of the 1 min OPC data points. Calculated scattering (top row) describes the sub-µ values well while coarse (and total) are overestimated by about 5-10%. This is expected to be a result of calibration sizing uncertainties of about 3% for the largest aerosol.

The absorption properties (panels D-I) are based upon refractory volumes and shown for two assumptions of refractory composition. The middle row assumes all of the refractory volume is pure absorbing BC with a refractive index of n =1.95 – 0.66i (not likely as per Figure 9 discussion). This assumption (middle row) shows that most of the data (including sub-µ) and the relationship corresponding to the TRACE data seen in Figure 6, lies well above the 1:1 line while a few of the dust cases lie below. The bottom row assumes the same refractive index for BC but only 50% of the refractory volume is BC. This yields an underestimate OPC derived sub-µ absorption for most of the data. If a 15% increase is added to the calculated OPC absorption (effect of BC on surface of aerosol, FMK) then the 1:1 line would fall through the TRACE regression line shown in Figure 6. Additional enhancements to absorption due to encapsulation of the BC (FMK) as suggested by Figure 14 would be consistent with underestimates for our calculated absorption (again assuming 60% of refractory mass is BC and modeled as an external mixture - panel H) when compared to the observed PSAP values for most data. The generally good agreement with the sub-µ absorption (H) is also consistent with the TRACE-P data except for the highest dust and pollution leg (green) on flight 13. Note that for this leg a better agreement for the 100% BC case (middle row) is evident for the sub-µ absorption case in Flight 13. We believe that this is a result of an increased loss of refractory OC to the dust increasing the BC fraction of the refractory mode but this analyis is beyond the scope of this paper and will be presented elsewhere. The coarse particle absorption is essentially the same for (F) and (I) plots and good agreement is evident for the 750 m dust case (red) on flight 13 while the 250 m case (green) is underestimated in the calculations. This may be a result of soot present on the coarse dust that is not accounted for in these calculations.

4.4 The influence of BC on dust optical properties

The optical properties described above for the accumulation and dust modes can be applied to our OES distributions for all data where we have thermally resolved size information. We apply this first to Figure 12 that used the variation in VAE with coarse

volume as evidence for soot attached to dust surfaces. In order to properly evaluate this we need to allow for the variation in dust VAE (and MAE) with size and for the effect of the impactor in separating out coarse particle absorption from sub-µ absorption. Because of the sigmoidal size cut (Wang and John, 1988) some BC/soot aerosol is also removed by the impactor and measured as coarse particle absorption. In order to clarify this, we have calculated the absorption for the coarse particles assuming they were the observed dust and accumulation mode aerosol (Figure 12B) excluded by the impactor. We also show results for the assumption that they are coarse dust exclusively (Figure 12C). The latter show a small increase above asymptotic values at low dust volumes. This is due to volume mean diameters decreasing at low concentrations to result in higher VAE values (Figure 13a). However, when we calculate the VAE that includes the BC and the dust excluded from the sub-µ PSAP by the impactor cut (and interpreted as coarse absorption) we obtain Figure 12B. This figure shows substantially more absorption influence on measured VAE values at lower coarse surface areas. Nevertheless, this absorption remains considerably less than in the measured values (Figure 12A).

Our best estimate of the actual enhanced absorption due to BC on the dust surface is given by the difference between measured VAE (Figure 12A) and estimated VAE values (Figure 12 B) as shown in Figure 12D. The low altitude leg on flight 13 had the highest dust with high pollution (BC) continues to show elevated VAE.About half of the other flights also exhibit elevated absorption for coarse surface volumes below 200 $\mu m^3 cm^{-3}$. Again, the positive and negative values evident at lowest volumes is a result of noise due to taking differences in total and sub-µ absorption over these short 1-2 minute intervals. Even so, these observations suggestthat optically measurable BC is commonly associated with dust in these environments. The degree to which BC attaches to dust will depend upon the concentrations of dust and BC, the time they are associated, whether dust was present at the points of combustion, possible cloud effects etc. such that the degree of association is expected to vary significantly. When Figure 12D is color coded for sub-µ absorption (not shown) it also demonstrates that largest positive values are generally associated with largest sub-µ absorption. For example, about 20% of the total BC is needed to account for the elevated values on coarse dust (green dots) for volumes above about 400 $\mu m^3 cm^{-3}$.

4.5 The influence of dust on BC optical properties

We discussed above the perturbation of dust optical properties arising from the coagulation of BC with the dust mode. However, the presence of dust surface area can also be expected to influence the condensation of vapors such as sulfuric acid and OC vapors. In the absence of dust these species commonly condense on the accumulation mode (and coarse pollution aerosol to contribute to the volatile aerosol discussed earlier, (eg. Figure 8). Because these species are commonly associated with the combustion source regions we might expect them to be found in characteristic ratios with BC for a given region and time. Also, because the BC component is formed at high temperatures in the combustion process, these condensates will be added to the BC after its emission. Condensates like combustion derived BC may promptly deposit to aerosol surface while others, like sulfates, would take longer because photochemical processes are involved. If

BC is generated and emitted into dusty air with elevated surface area, then significant fractions of these condensates can be expected to attach to the dust and thereby reduce the fraction typically associated with soot/BC in the accumulation mode.

Figure 16 shows the ratio of the refractory to total accumulation mode aerosol (dust removed) obtained from our OPC volatility data. This data is stratified to below 2km altitude and shown for over three decades of coarse particle volume along with average values binned over equal log intervals of coarse particle volume. There is little change in this ratio when coarse volume is below about 20 $\mu m^3 cm^{-3}$. This is expected due to the relatively large accumulation mode surface areas in these cases and because coarse pollution emission and accumulation mode emissions derived from regional combustion sources can be expected to trend together. However, when coarse volumes exceed this value it is generally due to the increased mixing of windblown dust with the pollution aerosol. The refractory soot volume clearly seen to be an increasingly greater fraction of the sub-μ accumulation mode aerosol as the dust volume increases. This is consistent with the increased relative uptake of condensates to the coarse dust surface. When this happens the relative mix of BC/soot increases relative to associated condensates in the accumulation mode.

We demonstrated earlier (Figures 4 and 7) that BC in refractory soot contributes only a small fraction of the total accumulation mode volume even though it dominates the absorption. Hence, the scattering properties of the accumulation mode are generally dominated by the volatile/soluble component often derived via condensation onto the soot aerosol. Consequently, when the relative fraction of the refractory component of the accumulation mode increases we can expect the value of sub-μ ϖ to decrease. This is shown to be the case in Figure 16 where the lowest sub-μ ϖ values are associated with the highest dust cases and highest refractory volume fraction present in the accumulation mode. Although the dust tail present in the sub-μ mode contributes aerosol with ϖ near 1 (see Figure 13), the reduction in scattering due to loss of condensate to the coarse dust mode has the greater effect. The result is lower measured sub-μ ϖ values than in the non-dust case even though ϖ for the total aerosol increases due to dust.

It is important to note that this process transfers this scattering mass from sub-μ sizes that have a maximum MSE to sizes with an MSE an order of magnitude lower (Figure 13a). As a result, the contribution to scattering extinction by these condensable emissions (eg. sulfate) is dramatically reduced. For example, the contributions of identical sulfur emissions to column optical depth will be reduced significantly as a result its uptake on the dust. At the same time sub-μ ϖ will be lowered compared to what might be expected if the pollution and dust modes were separately modeled with no interaction. Consequently, the optical properties of a mixture of dust and pollution aerosol are not cumulative and will be different if they mix before or after most condensates have been adsorbed.

This observation prompted us to model sub-μ ϖ values from the size distributions based upon the refractory fraction (external mix) of the accumulation mode evident in Figure 13 and the assumed 60% of BC mass in the sub-μ refractory OPC sizes. Calculated ϖ is generally higher than observed with greater differences evident at dust concentrations above about 100 um^{2}cm-^{3}. Values for ϖ are generally overestimated probably as a consequence of underestimating BC absorption due to modeling it as an external mix. However, the increasing difference at higher dust concentrations is also

possibly related to changes in our assumed constant BC fraction of refractory volume. This may also change in high dust concentrations due to loss of OC to the dust.

4.6 Column characteristics and Radiative Closure

One of the objectives of measurements is to use our OES data and volatility to assess the contributions of various aerosol components to optical properties at all times during these experiments. These are of particular interest when we can model these properties in conjunction with satellite spectral measurements of aerosol properties. A first step in this is to confirm that we can apply our approach above to generate profiles of column optical properties consistent with measured values. The data from the ascent profile just after 3:00 in Figure 10 is plotted vs. altitude here (Figure 17) to reveal both the variations in the size distributions and their impact upon scattering and absorption. The vertical profile of the aerosol area distribution (middle) and extinction (bottom) clearly indicate the dominance of coarse dust. The calculated and measured extinction and absorption (top) indicate excellent agreement for both except for one case of extinction calculated from the size distribution at 400 m. This is in the peak of the largest dust plume measured and this conspicuous underestimate is expected to be due to the largest sizes particle sizes not captured by the OPC and/or saturation of the OPC amplifier by largest sizes and associated electronic limitations. Otherwise, the measured scattering and absorption properties are well represented by the calculations on this flight (and others not shown, Kahn et al. 2003).

4.4 CCN and links to the size distributions and BC

The emission of BC and its association with volatile aerosol also impacts aerosol CCN in this region. Earlier we mentioned that the number of refractory BC aerosol for these experiments dominated the total aerosol number. This is also true for larger sizes in the accumulation mode. This is shown in Figure 18a where refractory CN are plotted against total number measured by the OPC for each horizontal leg on TRACE-P. A typical minimum in the number distribution is also commonly found near 0.08-0.10 μm due to processing of the larger sizes by non-precipitating clouds (Hoppel et al., 1986). An example of the OPC+DMA number distribution (inset) illustrates typical cases where it is clear that the distribution is primarily a single mode and that OPC sizes larger than 0.1 μm contribute about 70% of the total number, consistent with this figure. In any event, this lower limit provides definition of a CCNproxy that was shown to trend strongly with scattering. When lower number fractions occurred it was generally a result of infrequent cases of recent nucleation (volatile small aerosol) that were often rapidly depleted in a day or so through coagulation (McNaughton et al, submitted). We have also shown that the refractory soot/BC in the accumulation mode is generally associated with volatile constituents (Figure 4, 7) that are closely linked to the soluble species (Figure 8) implying that this mode will also be effective CCN after leaving the source areas. Hence, we argue that the refractory number distributions associated with BC aerosol determine most of the CCN population. Regions like these that are strongly influenced by sources of BC should have CCN and related cloud effects linked to the nature of the combustion process creating BC particle number.
Effective ambient CCN depend upon their size, composition and the typical values of supersaturation for clouds active in the region. However, it is of interest to explore the

implications of these observations to the characterization and even the possible remote sensing of these potential CCN by satellite. To illustrate this we describe a CCN_{proxy} as all particles measured by the OPC (larger than 0.1 μm) recognizing that in these regions these may be only 60-70% of the total potential CCN evident in Figure 18a. A plot of CCN_{proxy} for TRACE-P against measured aerosol light scattering demonstrates these particles usually dominate the light scattering (as well as absorption) of the aerosol. Data have been shaded to illustrate the dependence of this relationship on the calculated wavelength dependence of the light scattering (Angstrom exponent). The clear gradient in shading is important because satellites with spectral measurement of radiance can detect both the column optical depth (column integral of the scattering) and its wavelength dependence.

Relative increases in coarse aerosol (eg. dust) generally add little particle number to effective CCN (Figure 5c) but significantly increase scattering seen by satellite and drive the Angstrom exponent to approach zero. This has prompted the use of a so-called aerosol index (AI) based upon the product of the scattering and the non-dimensional Angstrom exponent, both capable of being inferred from satellite observations (Nakajima et al., 2001). The AI is designed to modify measured scattering by weighting it with Angstrom values that approach zero for coarse particle contributions. This AI biases the total scattering to be closer to scattering values for particles in the accumulation mode that dominate particle number. Figure 18b shows a plot of CCN_{proxy} vs. the AI generated from the TRACE-P size distributions over the horizontal legs. This shows a strong relationship even for this 90 sec data and demonstrates encouraging potential for retrieval of CCN from satellite. A proper evaluation of this approach requires adjusting our size distributions to ambient sizes based upon the volatility and solubility to get optical ambient optical properties and integrating results over the column and over spatial scales suitable for comparison. These and other considerations, including assessments of conditions when such retrievals can be effectively applied, will be dealt with in a future paper for both the TRACE-P and ACE-Asia data sets. This data demonstrates how the size distribution and its link to BC and associated condensates establishes a soluble number population directly linked both to optical properties and to CCN number. This relationship is strong because the range of particle sizes (Figure 18a, insert)dominating the number population and the scattering efficiency for the accumulation mode are similar as a result of the condensation of soluble species onto the BC.

5. Conclusion

Thermal analysis of the size distributions of Asian aerosol provided insight into its physio-chemical properties. This approach demonstrated that BC and associated high temperature emissions establish most of the aerosol number concentration by providing sites upon which other species (eg. sulfate, nitrate, water) condense and/or heterogeneously react. These soluble species and organic components were mixed with the soot and constituted most of the volatile fraction. TDMA data indicated that within the accumulation mode the refractory soot fraction was generally 10 to 25% of the total volume for sizes near 0.1 μm. This fraction increases with size within this mode while smaller volume fractions were present at smaller diameters consistent with growth via a condensation process.

The light absorption properties of the aerosol were dominated by BC and dust components. BC in the accumulation mode tended to have OES volume mean diameters near 0.3±0.2μm and close to the maximum in MAE values for BC. Most of the cases on ACE-Asia

and on TRACE-P exhibited a relation between absorption and scattering that was linear and implying a single scatter albedo for the accumulation mode of near 0.84 ±0.02 in the absence of dust. The size dependent MAE for these cases are based upon an assumed density of 1.9 g cm^{-3}. Mie calculations using the OPC refractory volume distributions and refractive index of 1.95 – 0.66i yield a size-weighted sub-μ MAE of about 4.7 m^{2}g^{-1} for the pure BC component when treated as BC spheres over the refractory OES size ranges. If a large fraction of these are aggregates of BC primary aerosol mass with sizes of 0.1 – 0.2 μm diameter then larger sizes would have properties more like the primary sizes and should increase overall MAE values to between 5 and 6 m^{2}g^{-1} (Figure 13a) as per FMK. If the BC were usually on the surface of the accumulations mode aerosol then an additional enhancement of 15% might raise average values to 6 to 7 m^{2}g^{-1}. Additional enhancements from some BC being encapsulated in OC and volatile aerosol at the 10-20% BC volume fraction level could also increase these values for certain sizes into the 10-15 m^{2}g^{-1} range under ideal conditions, as per FMK. However, if we allow for the probability of significant BC with lower refractive indices, the BC present at larger sizes, a variable range of morphology, a variable state of mixing, etc. then such high values appear unlikely. Consequently, based upon our volatility and size we estimate typical values for an effective MAE of BC in aged Asian pollution to be 8.5 m^{2}g^{-1} ± 3 m^{2}g^{-1} where much of this variability appears related to enhanced absorption from BC mixed with condensed species. This is close to the results of EC measurements aboard the C-130 and the most likely values estimated by FMK.

Optically effective dust sizes were measured out to 14μm. Selection of cases with minimum accumulation mode absorption provided determination of refractive indices for dust that were consistent with the measured absorption and scattering coefficients. These constraints imply refractive indices for pure dust were about n = 1.53 - 0.0005i (±0.0001i). Unlike BC, the MAE for dusts have a maximum near several micrometers. This results in ϖ values for the dust distribution that vary from about 1 for sub-μ sizes up to about 0.94 at 10μm diameter, consistent with the effective coarse particle ϖ values observed near 0.97 (Anderson et al. in press). Optical properties were well described by the presence of two modes, an accumulation mode with an ϖ near 0.84 ± 0.03and a dust mode with an ϖ near 0.96±0.01. Variations in relative contributions to both modes account for most of the variation in total ϖ observed. The statistically larger values for ϖ seen for Asian aerosol south of 25°N (TRACE-P) and those on ACE-Asia are explained by the greater prevalence of dust mixed with aerosol north of 25°N.

In cases of unusually high dust concentrations there was significantly greater measured sub-μ absorption present than could be accounted for by the dust or contributions from refractory BC in the sizes described above. The data suggests that BC and volatiles are accumulated onto the dust at sizes near 1-2 μm or so. In high dust cases up to 20% of the total BC appeared to be on the dust surface. While the net change in aerosol absorption may be of secondary importance, these events provide exceptions to the size depended absorption commonly seen for BC and indicate an additional role for dust.

Accumulation mode refractory volume fractions (soot/BC) were found to increase with dust concentrations along with an associated decrease in sub-μ ϖ values. Because sub-μ dust should increase ϖ this decrease appears to be due to the relative increase in the BC fraction of the accumulation mode as a result of uptake of condensates onto the dust. For a given source strength of condensates such as sulfates and OC, dust will result in a transfer of this scattering mass onto larger sizes with low effective MSE instead of onto the optically effective

accumulation mode, and thereby reducing the radiative effect per unit mass of condensate emitted. Hence, collection of both some BC through coagulation and the subsequent condensation of secondary aerosol on the dust results in size dependent changes in both sub-µ and supermicrometer aerosol optical properties.

The combined DMA and OPC data describe the complete size distribution from 0.007 to 14µm. This and the demonstrated link between volatility and solubility allow us to infer those sizes most likely to be CCN under typical conditions. Because the moments of this single mode can describe the number, area and volume it can also be used to describe the scattering. This provides a link between the number of CCN likely in this mode and the scattering. When integrated over the column the scattering describes the AOD seen by satellites and its spectral dependence. The observation made on TRACE and ACE-Asia demonstrate that under many conditions this descriptor relates well to CCNproxy and suggests it serves as a meaningful tool for satellite estimates of CCN. The observation that refractory BC provides the condensation site for most aerosol number implies that it is also responsible for the genesis of most CCN number. Consequently, BC is not only instrumental in contributing to the direct effect through determining ϖ but also is a key player in the indirect effect through establishing the CCN size spectrum. Hence, the nature of the combustion process and how BC emissions and the number of BC particles are generated has implications for both direct and indirect forcing. Moreover, the details of BC properties and its optical effects must be considered in conjunction with the full aerosol size distributions and the volatile condensates associated with it.

REFERENCES

Anderson, J.R., P.R. Buseck, T.L. Patterson, and R. Arimoto, Characterization of the Bermuda tropospheric aerosol by combined individual-particle and bulk-aerosol analysis, Atmos. Environ., v. 30, p. 319-338, (1996).

Anderson, T. L., D. S. Covert, S. F. Marshall, M. L. Laucks, R. J. Charlson, A. P. Waggoner, J. A. Ogren, R. Caldow, R. Holm, F. Quant, G. Sem, A. Wiedensohler, N. A. Ahlquist, and T. S. Bates, "Performance characteristics of a high-sensitivity, three-wavelength, total scatter/backscatter nephelometer", J. Atmos. Oceanic Technol. **13,** 967-986 (1996).

Bergstrom, R.W., Predictions of the spectral absorption absorption and extinction coefficients of an urban air pollution model, Atmos. Environ., 6, 247-258, 1972.

Berner, A., C. H. Lurzer, F. Pohl, O. Preining and P. wagner, The size distributions of urban aerosols in Vienna, Sci. Total Environ., 13, 245-261, 1979.

Bertram, T., B. Huebert, S. Howell, B. Blomquist, and J. Heath, Organic andelemental carbon vs. altitude during ACE-Asia, to be submitted JGR 2003.

Bond, T. C., T. L. Anderson and D. Campbell, "Calibration and intercomparison of filter-based measurements of visible light absorption by aerosols", Aerosol Sci. and Tech., **30**, 582-600, (1999).

Carmichael G. R., et al., "Regional-Scale Chemical Transport Modeling in Support of Intensive Field Experiments: Overview and Analysis of the TRACE-P Observations", Jour. Geophys. Res., submitted Dec. 2002.

Clarke, A. D. "A Thermo-optic technique for in-situ analysis of size-resolved aerosol physicochemistry", Atmos. Env., 25A, 3/4, 635-644, 1991.

Clarke, A.D. and J.N. Porter, Pacific Marine Aerosol Part II: Equatorial Gradients, Ammonium and Chlorophyll During SAGA3, Jour. Geophys. Res., 98, D9, 16,997-17,010, 1993

Clarke, A.D., T. Uehara and J. Porter, Atmospheric Nuclei and Related Aerosol Fields over the Atlantic: Clean Subsiding Air and Continental Pollution during ASTEX, Jour. Geophys. Res., D21, 25,821-25,292, 1997.

Clarke, A.D., W.G. Collins, P.J. Rasch, V.N. Kapustin, K. Moore, S. Howell, and H.E. Fuelberg, Dust and pollution transport on global scales: Aerosol measurements and model predictions, *Journal of Geophysical Research, 106* (D23), 32,555-32,569, 2001.

Clarke, A.D., V. Kapustin, A Pacific Aerosol Survey – Part 1: A Decade of Data on Production, Transport, Evolution and Mixing in the Troposphere, Jour. Atmos. Sci., v59, 3, Part 1, 2002.

Fuller, K., W. C. Malm and S. M.. Kriedenweis, Effects of mixing on extinction by carbonaceous particles, JGR, 104, 15,941-15,954, 1999.

Hoppel, W. ., G. M. Frick, and R. E. Larson, Effect of non-precipitating clouds on the aerosol size distribution in the marine boundary layer, Geophys. Res. Lett., 13, 125-128, 1986.

Huebert B.J., R.J. Charlson, Uncertainties in data on organic aerosols, Tellus Series B-Chemical And Physical Meteorology, 52 (5): 1249-1255 NOV 2000

Jacob, D. J., J. H. Crawford, M. M. Kleb, V. E. Connors, R. J. Bendura, J. L. Raper, et al..., "THE TRANSPORT AND CHEMICAL EVOLUTION OVER THE PACIFIC (TRACE-P) MISSION: DESIGN, EXECUTION, AND OVERVIEW OF RESULTS"(tracep_overview.pdf updated:12/02/2002 1.14 MB)

Kalashnikova, O.V., and I.N. Sokolik, Importance of shapes and compositions of wind-blown dust particles for remote sensing at solar wavelengths, *Geophysical Research Letters*, *29* (10), 38, 2002.

Kaufman, Y., D. Tanre, O. Dubovik, A. Karnieli and L. remer, Absorption of sunlight by dust as inferred by satellite measurements and ground based remoe sensing, GRL, 28, 1479-1482, 2001.

Koepke, P. and M. Hess, Scattering functions of tropospheric aerosols: the effects of nonspherical particles, Applied Optics, 27, 2422-2430, 1988.

Lim, H., B. J. Turpin, E. Edgerton, S.V. Hering, G. Allen, H. Maring an P. Soloman, Semicontinuous aerosol carbon measurements: Comparison of Atlanta supersite measurements, Jour. Geophys. Res., 108, D7, 8419, doi: 10,1029/2001JG001214, 2003.

Ma, Y., D. Orsini, K. Maxwell, Y. N. Lee, K. Moore, V. N. Kapustin, A. D. Clarke R. Weber, Refinements to the particle-into-liquid sampler (PILS) for ground and airborne measurements of water soluble aerosol chemistry, Submitted JGR Nov. 2002.

Maenhaut, W., Ptasinski J. and J. Cafmeyer, Detailed mass size distributions of atmospheric aerosol species in the Negev desert, Israel, during ARACHNE-96, 422-427, Nuclear Inst. and Methods in Physics Research B 150, 1999.

Mayol-Bracero, O.L., R. Gabriel, M.O. Andreae, T.W. Kirschstetter, T. Novakov and D.G. Streets, Carbonaceous Aerosol over the Indian Ocean during INDOEX: Chemical Characterization, Optical Properties and Probable Sources, Jour. Geophys. Res . in press 2002.

McNaughton et al., The spatial distribution and size evolution of particles in Asian outflow: the significance of primary and secondary aerosols during ACEAsia and TRACE-P, Jour. Geophys. Res., submitted.

Mishchenko, M.I., L.D. Travis, R.A. Kahn, and R.L. West, Modeling phase functions for dustlike tropospheric aerosol using a shape mixture of randomly oriented polydisperse spheroids, Jour. Geophys. Res ., 102, 16,831-16,847, 1997.

Nakajima, T., A. Higurashi, K. Kawamoto and J. Penner, A possible correllation between satellite-derived cloud and aerosol microphysical parameters, GRL, 28, 1171-1174, 2001.

Orsini, D., Y. Ma, A. Sullivan, B. Sierau, K. Baumann, and R. Weber, Refinements to the Particle-Into-Liquid Sampler (Pils) For Ground and Airborne Measurements Of Water Soluble Aerosol Composition, Atm. Environ., in press, 2003.

Posfai, M., J.R. Anderson, P.R. Busek and H. Sievering, Soot and sulphate aerosol in particles in the remote atmosphere, Jour. Geophys. Res., 104. 21,685-21,693.

Posfai, M., R. Simonics, J. Li, P.V. Hobbs and P.R. Busek, Individual aerosol particles from biomass burning in southern Africa: 1. Compositions and size-distributions ofr carbonaceous particles, J. Geophys. Res. Vol. 108 No. D13, 10.1029/2002JD002291, 08 March 2003

Pinnick, R. G., J.D. Pendelton and G. Videen, Response characteristics of particle measurement systems active scattering spectrometer probes, Aerosol. Sci. and Tecnol., 33, 334-352, 2000.

Saathoff, H., C. Linke, O. Möhler, K. H. Naumann, M. Schnaiter, W. Schöck, R. wagner, and U. Schurath, Influence of Coatings on Structure and Optics of Soot Aerosol, poster IGAC conference 2002, 18-25 September 2002, Crete, Greece. [http://imk-aida.fzk.de/abstract/]

Seinfeld, J. and S. Pandis, *Atmospheric Chemistry and Physics*, John Wiley and Sons, NY, p429, 1998.

Smith M H and C D O'Dowd. "Observations of accumulation mode aerosol composition and soot carbon concentrations by means of the high-temperature volatility technique". J Geophys Res, 101, D14, 19,583-19,591, 1996.

Sokolic, I.N. and O. B. Toon, Incorporation of mineralogical composition into models of the radiative properties of mineral aerosol form UV to IR wavelengths, JGR, 104, 9423-9444, 1999.

Schütz, L., Long range transport of desert dust with special emphasis on the Sahara, Annals of the New York Academy of Science, in AEROSOLS: ANTHROPOGENIC AND NATURAL SOURCES AND TRANSPORT, eds. T. Kniep and P. Lioy, 515-532, 1980.

Wang, H. C. and W. John, Characteristics of the Berner Impactor for Sampling Inorganic Ions, Aerosol Sci. and Tech., 8, 157-172, 1988

Weber, R.J., D. Orsini, Y. Daun, Y.-N. Lee, P. Klotz, and F. Brechtel, Aparticle-into-liquid collector for rapid measurements of aerosol chemical composition, Aerosol Sci. Tech., 35, 718-727, 2001.

Weber, R. J., S. Lee, G. Chen, B. Wang, V. Kapustin, K. Moore, A. D. Clarke, L. Mauldin, E. Kosciuch, C. Cantrell, F. Eisele, D. C. Thornton, A. R. Bandy, G. W. Sachse, H.

E. Fuelberg; New Particle Formation in Anthropogenic Plumes Advecting from Asia Observed During TRACE-P

Woodward, S., Modeling the atmospheric life cycle and radiative impact of mineral dust in the Hadley Centre climate model, *Journal of Geophysical Research*, *106* (D16), 18,155-18,166, 2001.

LIST OF FIGURES (to revise)

with elevated absorption in Figure 2. Bottom panels show TandemDMA thermal analysis for three cases of size-selected aerosol. [see text for details]

8. An example of a comparison of aerosol volatility results with PILS data for TRACE-P flight 14. (a) Conversion of OPC OES aerosol diameters to estimated actual diameters Heavy colored lines) for sizes expected to be detected by PILS size cut (black line) from those measured by OPC (light colored lines). (b) Continuous values of resulting total OPC derived mass (blue line) and refractory mass (black shaded) are shown with PILS soluble mass superimposed upon the refractory mass. Note excellent agreement in variations and in concentrations to within about 20%. Difference will be due in part to volatile species undetected by PILS including expected organic carbon and others.

9. Relationships between absorption of BC, EC and refractory volume over sample periods for EC of about 30min. Slopes are indicated as B and the R values for correlation are indicated. Correlation between PSAP absorption and refractory OPC volumes are highest with R^2 of 0.75 while between EC and PSAP absorption and between EC and refractory soot volume have R^2 of only about 0.25 and 0.3 respectively reflecting in part the lower signal/noise for the EC measurements. The MAE values from the slope of the regression for absrption vs. EC (9a) range from 6.5 m^2g^{-1} (sub-μ) to 8.7 m^2g^{-1} for total aerosol.

10. Comparison of measured and modeled coarse and sub-μ scattering and absorption for ACE-Asia flight 13. Best fit to measured total and sub-μ scattering (top) and absorption (middle) in high dust is based on OES OPC sizes for refractive index of n = 1.54 – 0.0005i. Total absorption agrees well but sub-μ absorption is about 30-40% low during peak dust scattering periods but agrees well at lower dust concentrations (eg. after 6:00). Values for total measured and calculated ϖ agree well but sub-μ values are high during highest dust periods as a result of the low calculated absorption (see text for details).

11. SEM images for the three flight altitudes (Top-5,500 m; Middle-700 m; Bottom-250 m) on flight 13 discussed at various places throughout text. White bars at bottom are 2um long. Some particles identified by emission spectra are labeled for reference. Square – various forms of aluminosilicates, Triangle – Calcium carbonates; Open circle – large spherical graphitic carbon; Closed circle – more typical soot carbon aggregates. All small unlabeled spherical particles are also graphitic soot (BC) and almost all carbon particles were originally associated with volatile material that has been vaporized by the high density SEM electron beam. Note unusually large graphitic spheres that are at low concentrations but more prevalent in this region than many others and the large aggregated BC cluster in center panel. Soot particles are present at all altitudes and seen attached to dust but relative concentrations of soot increase significantly at lowest altitudes. [see text for details].

12. Coarse particle volume absorption efficiency (VAE) vs. coarse particle OES volume Flight 13 flight legs highlighted. A) as measured; B) calculated based upon impactor transmission that includes some accumulation mode in coarse mode; C) calculated values assuming only dust in coarse mode; D) the difference between measured (A) and

modeled (B) VAE values to get excess coarse absorption associated with coarse aerosol and presumed to reflect BC attached to dust surface and larger BC (see text).

13. (a) An example of size dependent MSE and MAE properties modeled based upon indicated refractive indices for dust and BC. (b) Size dependent ϖ for same dust and BC shown in (a) and a mix of BC with non-absorbing volatiles similar to ACE aerosol.

14. (a) Plot of VAE of the refractory OEV volume vs. ratio of volatile to refractory OEV volumes (dust removed). (b) Plot of VAE vs. ratio of OC plus non-sea-salt sulfate to refractory OEV volume (dust removed). As the volatile to refractory component in the accumulation mode increases so does the absorption per unit refractory component suggesting an absorption increase per unit BC as the volatile fraction increases.

15. Comparison of measured (nephelometer and PSAP) and calculated values for total, sub-μ and coarse aerosol properties for scattering (top) absorption assuming a100% OES volume is pure BC (middle panels) and assuming only 50% of volume is pure BC (bottom panels). Flight 13 legs from Figure 10 are indicated in color. Refractive index of dust (n = 1.54 – 0.0005i) and BC (n=1.95-0.66i) is used. The high calculated OPC absorption values above the 1:1 line are a result of modeling the refractory low absorbing aerosol shown in Figure 6 as absorbing BC. Low relative OPC absorption below the 1:1 line (calculated for sub-μ refractory soot only) is due to the soot in the coarse mode (on dust etc.) not captured by model.

16. Plots of the refractory soot fraction of the accumulation mode volume (Vsoot/Vsub) and sub-μ ϖ as a function of coarse dust volume (Vcoa) (OEV) for entire ACE-Asia experiment. As Vsoot/Vsub increases there is less scattering by condensates on the sub-μ soot due to uptake onto coarse aerosol. This result in lower the sub-μ ϖ values. Dashed line is the hypothesized BC fraction in the refractory accumulation mode (see text).

17. Application of the above aerosol optical properties to the rapid vertical profile in flight 13 (Figure 10 3:10-3:30) to the OPC size distribution. Total absorption and extinction are compared to measured (nephelometer and PSAP) data as part of column closure studies (see text). Vertical profiles of size resolved aerosol surface area and extinction are also shown.

18. The CCN proxy is defined here as those aerosol with OES larger then 0.1 as measured by the OPC. The top figure shows that these are directly related to the refractory CN number determined by BC (CN@300°C). The insert shows number size distributions that confirm how these sizes dominate the number distribution. Because these are also optically effective sizes the CCN$_{proxy}$ is also linearly related to scattering depending upon the value of the Angstrom exponent (middle). The product of the Angstrom exponent and the scattering defines the aerosol index (AI, measurable from satellite) that displays a strong linear relation to the CCN$_{proxy}$.